

DESCRIPTION

POSITIVE RADIATION-SENSITIVE RESIN COMPOSITION

TECHNICAL FIELD

5 The present invention relates to a positive
radiation-sensitive resin composition preferably used for
producing a plated shaped article, a transfer film using
the composition and a process for producing a plated
shaped article.

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BACKGROUND ART

As integrated circuit devices have been made finer,
higher integration of large scale integrated circuits
(LSI) and shifting to application specific integrated
15 circuits (ASIC) have been rapidly promoted recently. On
that account, a multi-pin thin film mounting process for
mounting LSI on electronic equipment is required, and
bare chip mounting by a tape automated bonding (TAB)
system or a flip chip system has been adopted. In such a
20 multi-pin thin film mounting process, a protruded
electrode having a height of not less than 10 μm that is
called a bump needs to be arranged as a connecting
terminal on a substrate with high precision.

Such a bump is produced by the following process at present. First, a barrier metal that becomes an electrically conductive layer is laminated on a wafer that has been worked as a LSI device, and then a
5 radiation-sensitive resin composition, i.e., so-called a resist, is applied and dried. Subsequently, the resist is irradiated with radiation (referred to as "exposure" hereinafter) through a mask so as to form an opening corresponding to the place where a bump is to be formed,
10 and then the resist is developed to form a pattern. Thereafter, using the pattern as a mold, electroplating is performed to deposit an electrode material such as gold or copper. Then, the resin portion is stripped, and the barrier metal is removed by etching. Thereafter, a
15 square chip is cut out from the wafer, followed by a mounting process, such as packaging (e.g., TAB) or a flip chip system.

In a series of steps of the above process for producing a bump, the following properties are required
20 for the resist.

(1) The resist can form a coating film having a uniform thickness of not less than 20 μm .

(2) In order to cope with narrowing of a pitch between bumps, the resist exhibits high resolution.

(3) The pattern that becomes a mold has an almost perpendicular sidewall, and the pattern has fidelity to the mask dimension.

(4) In order to enhance production efficiency of the
5 process, the resist has high sensitivity and excellent developability.

(5) The resist exhibits excellent wettability by a plating solution.

(6) The resist component is not eluted into a
10 plating solution in the plating step, so that it does not deteriorate the plating solution.

(7) The resist has high adhesion to a substrate so that the plating solution should not be introduced into the interface between the substrate and the resist in the
15 plating step.

(8) After plating, the resist can be easily stripped by a stripping solution.

Moreover, the resulting deposit needs to have the following properties.

20 (9) To the deposit, the shape of the pattern that is a mold has been transferred with fidelity, and the deposit has fidelity to the mask dimension.

As the resist for forming a bump, a positive radiation-sensitive resin composition containing a

novolak resin and a naphthoquinonediazide group-containing compound as main components has been heretofore employed (see, e.g., patent document 1). In this case, however, there is a problem that even if a
5 resist composed of the composition is developed, the resulting pattern is in such an inclined shape (tapered shape) that the pattern is tapered off to the resist surface from the substrate surface, and a pattern having a perpendicular sidewall is not obtained. Further, there
10 is another problem that because of low sensitivity of the resist, the exposure time is prolonged and the production efficiency is low. Furthermore, it cannot be said that the composition is satisfactory in the resolution and the fidelity of a deposit of a large thickness to the mask
15 dimension.

Patent document 1: Japanese Patent Laid-Open
Publication No. 207067/1998

DISCLOSURE OF THE INVENTION

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PROBLEM TO BE SOLVED BY THE INVENTION

It is an object of the present invention to provide a production process capable of precisely producing a plated shaped article of a large thickness such as a bump or a wiring, a positive radiation-sensitive resin

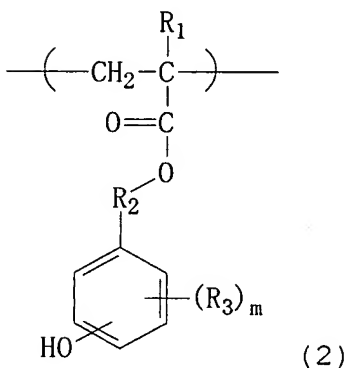
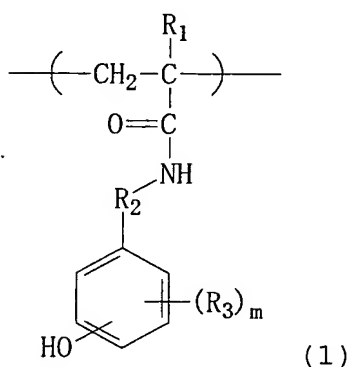
composition which is preferably used for the process and has excellent sensitivity and resolution, and a transfer film using the composition.

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MEANS TO SOLVE THE PROBLEM

The positive radiation-sensitive resin composition according to the present invention comprises:

- (A) a polymer containing structural units (a) represented by the following formula (1) and/or the following formula (2) and an acid-dissociable functional group (b),

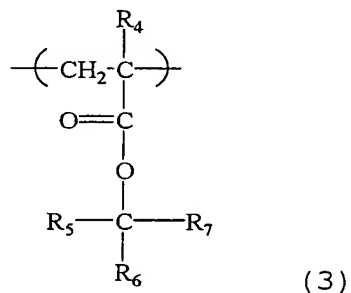


wherein R_1 is a hydrogen atom or a methyl group, R_2 is $-(CH_2)_n-$, n is an integer of 0 to 3, R_3 is an alkyl group of 1 to 4 carbon atoms, and m is an integer of 0 to 4,

(B) a component which generates an acid by
5 irradiation with radiation, and

(C) an organic solvent.

The acid-dissociable functional group (b) is preferably represented by the following formula (3):



10 wherein R_4 is a hydrogen atom or a methyl group, R_5 to R_7 are each an alkyl group of 1 to 4 carbon atoms, an alicyclic hydrocarbon group of 4 to 20 carbon atoms, an aromatic group or a substituted hydrocarbon group wherein at least one hydrogen atom in any one of these
15 hydrocarbon groups is replaced with a polar group other than a hydrocarbon group, R_5 to R_7 may be the same or different, and when any two of R_5 to R_7 are alkyl groups or substituted alkyl groups, their alkyl chains may be bonded to each other to form an alicyclic hydrocarbon

group of 4 to 20 carbon atoms or a substituted alicyclic hydrocarbon group.

The composition of the invention is preferably used for producing a plated shaped article, particularly a
5 bump.

In the composition of the invention, the component (B) is preferably contained in an amount of 0.1 to 20 parts by weight based on 100 parts by weight of the component (A), and the component (C) is preferably
10 contained in an amount of 20 to 80 parts by weight based on the total weight 100 parts by weight of the positive radiation-sensitive resin composition.

When a resin film having a film thickness of not less than 50 μm is formed from the resin composition, an
15 acid dissociation product obtained by dissociation of the acid-dissociable functional group (b) by the use of an acid preferably has a boiling point at 1 atm of not lower than 20°C.

The positive radiation-sensitive resin composition
20 of the invention may further comprise an alkali-soluble resin other than the polymer (A). The composition may further comprise an acid diffusion controller.

The transfer film according to the present invention has a resin film composed of the above-mentioned resin

composition. The resin film preferably has a film thickness of 20 to 200 μm .

The process for producing a plated shaped article according to the present invention comprises:

- 5 (1) a step of forming a resin film composed of the positive radiation-sensitive resin composition on a wafer having a barrier metal layer,
- (2) a step of exposing the resin film and then developing the resin film to form a pattern,
- 10 (3) a step of depositing an electrode material by electroplating using the pattern as a mold, and
- (4) a step of stripping the remaining resin film and then removing the barrier metal by etching.

15 EFFECT OF THE INVENTION

By the use of the positive radiation-sensitive composition of the invention, a pattern that becomes a mold for electroplating can be formed with fidelity to the mask dimension. Further, to the composition, the shape of a pattern that becomes a mold can be accurately transferred even in the electroplating step, and the composition can form a plated shaped article having fidelity to the mask dimension and has excellent sensitivity and resolution. Accordingly, the positive

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radiation-sensitive composition of the invention can be extremely preferably used for producing a plated shaped article of a large thickness such as a bump or a wiring of an integrated circuit device. In particular, the
5 positive radiation-sensitive resin composition having a structural unit represented by the chemical formula (1) exhibits excellent resolution performance on a copper sputtered substrate.

10 BEST MODE FOR CARRYING OUT THE INVENTION

The positive radiation-sensitive resin composition of the invention comprises (A) a polymer containing a specific structural unit (a) and an acid-dissociable functional group (b) which is dissociated by an acid and
15 becomes acidic, (B) a component which generates an acid by irradiation with radiation and (C) an organic solvent.

The positive radiation-sensitive resin composition of the invention contains a component which generates an acid upon exposure (referred to as an "acid generator"
20 hereinafter). When an acid is generated by exposure, chemical reaction (e.g., change of polarity, decomposition of chemical bonding, or the like) takes place in a resin film (i.e., resist film) composed of the positive radiation-sensitive resin composition by virtue

of a catalytic action of the acid, and the solubility of the resist in a developing solution is changed in the exposed portion. By making the best use of this phenomenon, the positive radiation-sensitive resin composition of the invention forms a pattern that becomes a mold for electroplating.

The mechanism of the pattern formation is further described below. When an acid generator is exposed, an acid is generated. By virtue of a catalytic action of the acid, the acid-dissociable functional group contained in the positive radiation-sensitive resin composition undergoes reaction, and thereby, it not only becomes an acidic functional group but also forms an acid dissociation product. As a result, solubility of the exposed polymer portion in an alkali developing solution is increased. The reaction of the acid-dissociable functional group is accelerated by carrying out heating (i.e., post exposure bake, referred to as "PEB" hereinafter) after exposure. The acid newly generated by the reaction of the acid-dissociable functional group acts as a catalyst on the reaction of another acid-dissociable functional group, whereby reaction of an acid-dissociable functional group and generation of an acid are "amplified" one after another. By making the

best use of such a chemical amplification action, a given pattern is formed with high sensitivity (i.e., small quantity of light for exposure) and high resolution.

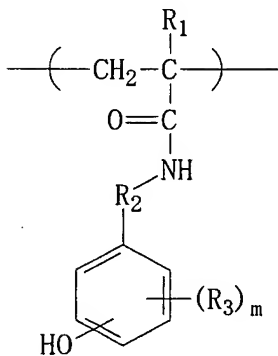
The alkali developing solution used for developing the exposed resist film can be prepared by dissolving one or more kinds of alkaline compounds in water or the like. After the development using the alkali developing solution, washing with water is usually carried out.

Polymer (A)

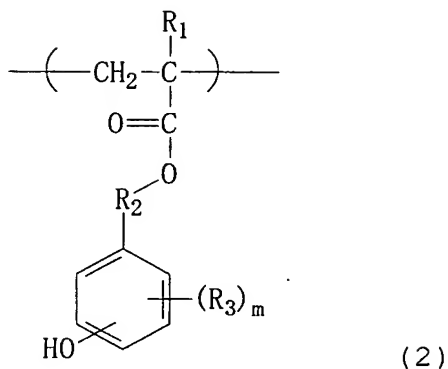
The polymer (A) for use in the invention is a polymer comprising the below-described structural units (a) represented by the formula (1) and/or the formula (2) and an acid-dissociable functional group (b).

Structural unit (a)

The polymer (A) has structural units represented by the following formula (1) and/or the following formula (2):



(1)



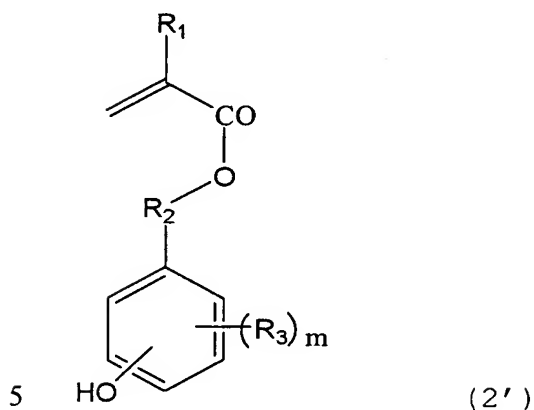
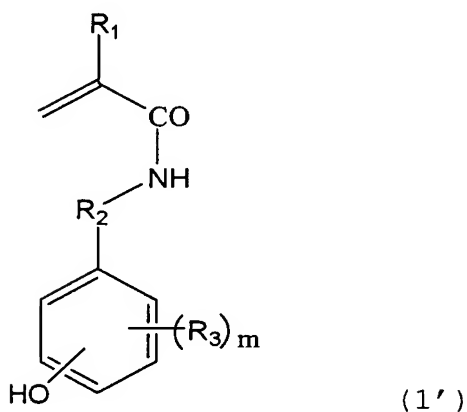
wherein R_1 is a hydrogen atom or a methyl group, R_2 is $-(\text{CH}_2)_n-$, n is an integer of 0 to 3, R_3 is an alkyl group of 1 to 4 carbon atoms, and m is an integer of 0 to 4.

5 Because the structural units represented by the formula (1) and/or the formula (2) are contained in the polymer (A), an effect of increasing adhesion of the resist to a substrate and thereby preventing introduction of a plating solution into the interface between the
 10 substrate and the resist in the plating step is exerted. Further, by controlling the type and the number of substituents contained in the structural unit, degree of acidity of the phenolic hydroxyl group can be changed, and hence, solubility of the composition of the invention
 15 in an alkali developing solution can be controlled.

Monomer (1') and monomer (2')

The structure of the formula (1) can be obtained by polymerizing a monomer (1') represented by the following formula to form the polymer (A). The structure of the

formula (2) can be obtained by polymerizing a monomer (2') represented by the following formula to form the polymer (A).



In the above formulas, R_1 is a hydrogen atom or a methyl group, R_2 is $-(\text{CH}_2)_n-$, n is an integer of 0 to 3, R_3 is an alkyl group of 1 to 4 carbon atoms, and m is an integer of 0 to 4.

10 Examples of the monomers (1') include amide group-containing vinyl compounds, such as p-hydroxyphenyl acrylamide, p-hydroxyphenyl methacrylamide, o-

hydroxyphenyl acrylamide, o-hydroxyphenyl methacrylamide, m-hydroxyphenyl acrylamide, m-hydroxyphenyl methacrylamide, p-hydroxybenzyl acrylamide, p-hydroxybenzyl methacrylamide, 3,5-dimethyl-4-hydroxybenzyl acrylamide, 3,5-dimethyl-4-hydroxybenzyl methacrylamide, 3,5-tert-butyl-4-hydroxybenzyl acrylamide, 3,5-tert-butyl-4-hydroxybenzyl methacrylamide, o-hydroxybenzyl acrylamide and o-hydroxybenzyl methacrylamide.

10 Examples of the monomers (2') include (meth)acrylic esters, such as p-hydroxyphenyl (meth)acrylate, o-hydroxyphenyl (meth)acrylate, m-hydroxyphenyl (meth)acrylate, p-hydroxybenzyl (meth)acrylate, 3,5-dimethyl-4-hydroxybenzyl (meth)acrylate, 3,5-tert-butyl-4-hydroxybenzyl (meth)acrylate and o-hydroxybenzyl (meth)acrylate.

20 Of the above monomers (1') and (2'), preferable are p-hydroxyphenyl acrylamide, p-hydroxyphenyl methacrylamide, 3,5-dimethyl-4-hydroxybenzyl acrylamide, 3,5-dimethyl-4-hydroxybenzyl methacrylamide, p-hydroxyphenyl methacrylate and p-hydroxybenzyl methacrylate.

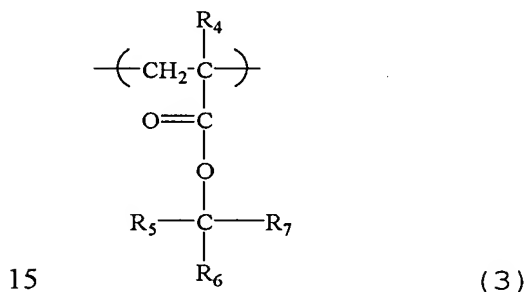
 The monomers (1') or the monomers (2') can be used singly or as a mixture of two or more kinds. Further,

the monomer (1') and the monomer (2') may be used in combination.

Acid-dissociable functional group (b)

The acid-dissociable functional group (b) contained
 5 in the polymer (A) is not specifically restricted as long
 as it is dissociated by an acid to form an acidic
 functional group. The acid-dissociable functional group
 (b) is, for example, a functional group that is
 dissociated by an acid to form a carboxyl group or a
 10 functional group that is dissociated by an acid to form a
 phenolic hydroxyl group.

Of such acid-dissociable functional groups (b),
 preferable is a functional group represented by the
 following formula (3):

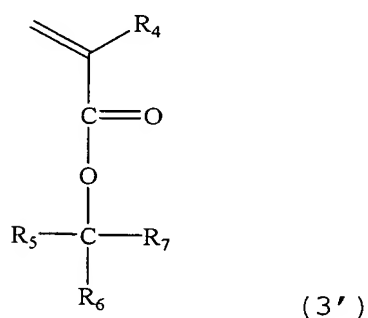


wherein R₄ is a hydrogen atom or a methyl group, R₅ to R₇
 are each an alkyl group of 1 to 4 carbon atoms, an
 alicyclic hydrocarbon group of 4 to 20 carbon atoms, an
 aromatic group or a substituted hydrocarbon group wherein
 20 at least one hydrogen atom in any one of these

hydrocarbon groups is replaced with a polar group other than a hydrocarbon group, R_5 to R_7 may be the same or different, and when any two of R_5 to R_7 are alkyl groups or substituted alkyl groups, their alkyl chains may be
 5 bonded to each other to form an alicyclic hydrocarbon group of 4 to 20 carbon atoms or a substituted alicyclic hydrocarbon group.

Monomer (I)

The polymer having such an acid-dissociable
 10 functional group (b) can be obtained by, for example, polymerizing a monomer (I) having an acid-dissociable functional group. For example, the structure of the formula (3) can be obtained by polymerizing a monomer ($3'$) represented by the following formula to form the
 15 polymer (A).



In the above formula, R_4 is a hydrogen atom or a methyl group, R_5 to R_7 are each an alkyl group of 1 to 4 carbon atoms, an alicyclic hydrocarbon group of 4 to 20 carbon atoms, an aromatic group or a substituted
 20 carbon atoms, an aromatic group or a substituted

hydrocarbon group wherein at least one hydrogen atom in any one of these hydrocarbon groups is replaced with a polar group other than a hydrocarbon group, R_5 to R_7 may be the same or different, and when any two of R_5 to R_7 are
5 alkyl groups or substituted alkyl groups, their alkyl chains may be bonded to each other to form an alicyclic hydrocarbon group of 4 to 20 carbon atoms or a substituted alicyclic hydrocarbon group.

In the formula (3'), R_5 to R_7 are each an alkyl group
10 of 1 to 4 carbon atoms, an alicyclic hydrocarbon group of 4 to 20 carbon atoms, an aromatic group or a substituted hydrocarbon group wherein at least one hydrogen atom in any one of these hydrocarbon groups is replaced with a polar group other than a hydrocarbon group.

15 Examples of the alkyl groups of 1 to 4 carbon atoms include methyl, ethyl, n-propyl, i-propyl, n-butyl, 2-methylpropyl, 1-methylpropyl and t-butyl.

Examples of the alicyclic hydrocarbon groups of 4 to 20 carbon atoms include cycloalkyl groups, such as
20 cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl; and groups derived from bridged hydrocarbons, such as adamantane, bicyclo[2.2.1]heptane, tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecane and tricyclo[5.2.1.0^{2,6}]decane. When any two of R_5 to R_7 are

alkyl groups, their alkyl chains may be bonded to each other to form an alicyclic hydrocarbon group of 4 to 20 carbon atoms, and examples of the alicyclic hydrocarbon groups thus formed include the same alicyclic hydrocarbon groups as described above.

Examples of the aromatic groups include phenyl, o-tolyl, m-tolyl, p-tolyl, 4-t-butylphenyl, 1-naphthyl and benzyl.

Examples of the polar groups other than hydrocarbon groups in the substituted hydrocarbon group, with which a hydrogen atom can be replaced, include:

chloro group; hydroxyl group; carboxyl group; oxo group (i.e., =O group);

hydroxyalkyl groups, such as hydroxymethyl, 1-hydroxyethyl, 2-hydroxyethyl, 1-hydroxypropyl, 2-hydroxypropyl, 3-hydroxypropyl, 2-hydroxybutyl, 3-hydroxybutyl and 4-hydroxybutyl;

alkoxyl groups of 1 to 6 carbon atoms, such as methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, 2-methylpropoxy, 1-methylpropoxy and t-butoxy;

cyano group; and

cyanoalkyl groups of 2 to 6 carbon atoms, such as cyanomethyl, 2-cyanoethyl, 3-cyanopropyl and 4-cyanobutyl.

Examples of such monomers (3') include t-butyl (meth)acrylate, 1,1-dimethylpropyl (meth)acrylate, 1,1-dimethylbutyl (meth)acrylate, 2-cyclohexylpropyl (meth)acrylate, 1,1-dimethylphenyl (meth)acrylate, 5 tetrahydropyranyl (meth)acrylate, 2-t-butoxycarbonylmethyl (meth)acrylate, 2-benzyloxycarbonylethyl (meth)acrylate, 2-methyladamantyl (meth)acrylate, 1,1-dimethyl-3-oxobutyl (meth)acrylate and 2-benzylpropyl (meth)acrylate.

10 As the monomer (I), a monomer which is dissociated by an acid to form a phenolic hydroxyl group is also employable.

Examples of such monomers include hydroxystyrenes protected by an acetal group, such as p-1-15 methoxyethoxystyrene and p-1-ethoxyethoxystyrene; t-butoxystyrene, and t-butoxycarbonyloxystyrene.

The acid-dissociable functional group (b) of the polymer (A) undergoes reaction by means of an acid to form not only an acidic functional group but also an acid 20 dissociation product. For example, in the case where 2-benzylpropyl (meth)acrylate is used as the monomer (I) to introduce the acid-dissociable functional group (b) into the polymer (A), the resulting acid dissociation product is 2-benzylpropene.

If the boiling point of the acid dissociation product at 1 atm (referred to as a "boiling point" simply hereinafter) is not higher than room temperature, an evil influence is liable to be exerted on the pattern shape in the production of a plated shaped article.

In the case where the thickness of the resist film is in the range of about 1 to 50 μm as in the case of forming a circuit of an integrated circuit device, even an acid dissociation product having a boiling point of lower than 20°C generally penetrates the resist film as a gas component in the PEB step, so that the acid dissociation product does not actually exert an influence on the pattern shape. In the production of a bump or the like, however, the thickness of the resist film must be sometimes made not less than 50 μm . In the case where the thickness of the resist film must be made not less than 50 μm , a gas component generated remains in the resist film and forms large bubbles. As a result, the pattern shape is liable to be markedly impaired when the resist is developed. On this account, when the acid dissociation product has a low boiling point, particularly a boiling point of lower than 20°C, it is difficult to apply the composition to uses where the thickness of the resist film exceeds 50 μm .

Accordingly, the monomer (I) is preferably a monomer by the use of which the acid dissociation product formed from the polymer (A) has a boiling point of not lower than 20°C. Examples of such monomers include 1,1-
5 dimethyl-3-oxobutyl (meth)acrylate, 2-benzylpropyl (meth)acrylate, 2-cyclohexylpropyl (meth)acrylate and 1,1-dimethylbutyl (meth)acrylate. Of these, 1,1-dimethyl-3-oxobutyl (meth)acrylate or 2-benzylpropyl (meth)acrylate is preferable. The acid dissociation
10 product derived from the 1,1-dimethyl-3-oxobutyl (meth)acrylate is 4-methyl-4-penten-2-one, and its boiling point is about 130°C. The acid dissociation product derived from the 2-benzylpropyl (meth)acrylate is 2-benzylpropene, and its boiling point is about 170°C.
15 The above monomers (I) can be used singly or as a mixture of two or more kinds.

For preparing the polymer (A), a copolymerizable monomer (referred to as a "monomer (II)" hereinafter) other than the monomers (1'), (2') and (I) may be also
20 copolymerized.

Examples of the monomers (II) include:

aromatic vinyl compounds, such as o-hydroxystyrene, m-hydroxystyrene, p-hydroxystyrene, p-isopropenylphenol,

styrene, α -methylstyrene, p-methylstyrene and p-methoxystyrene;

hetero atom-containing alicyclic vinyl compounds, such as N-vinylpyrrolidone and N-vinylcaprolactam;

5 cyano group-containing vinyl compounds, such as acrylonitrile and methacrylonitrile;

conjugated diolefins, such as 1,3-butadiene and isoprene;

amide group-containing vinyl compounds, such as
10 acrylamide and methacrylamide;

carboxyl group-containing vinyl compounds, such as acrylic acid and methacrylic acid; and

(meth)acrylic esters, such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, n-butyl
15 (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, glycerol mono(meth)acrylate, phenyl (meth)acrylate, benzyl (meth)acrylate, cyclohexyl
20 (meth)acrylate, isobornyl (meth)acrylate and tricyclodecanyl (meth)acrylate.

Of the above monomers (II), preferable are p-hydroxystyrene, p-isopropenylphenol, styrene, acrylic acid, methacrylic acid, methyl (meth)acrylate, ethyl

(meth)acrylate, n-butyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, benzyl (meth)acrylate and isobornyl (meth)acrylate.

The monomers (II) can be used singly or as a mixture
5 of two or more kinds.

The content of the acid-dissociable functional group (b) is not specifically restricted provided that it is within the limits not detrimental to the effect of the present invention.

10 In the case where the acid-dissociable functional group (b) is derived from the monomer (I), the ratio of the units derived from the monomer (I) contained in the polymer (A) to the units derived from other monomers than the monomer (I) is not specifically restricted provided
15 that it is within the limits not detrimental to the effect of the present invention. However, the weight ratio of the units derived from the monomer (I) to the total of the units derived from the monomers (1') and (2') and the units derived from the monomer (II), namely,
20 monomer (I)/(monomer (1') + monomer (2') + monomer (II)), is in the range of usually 5/95 to 95/5, preferably 10/90 to 90/10, more preferably 20/80 to 80/20.

If the ratio of the units derived from the monomer (I) is less than the lower limit of the above range, the

proportion of the resulting acidic functional group is low, so that the solubility of the resulting polymer in an alkali developing solution is lowered, and as a result, pattern formation sometimes becomes difficult.

5 The polymer (A) can be prepared by, for example, directly copolymerizing the monomer (1') and/or the monomer (2'), the monomer (I), and if necessary, the monomer (II).

10 The polymerization can be carried out by a radical polymerization process. As the polymerization initiator, a usual radical polymerization initiator is employable. Examples of the polymerization processes include emulsion polymerization, suspension polymerization, solution polymerization and bulk polymerization. Of these,
15 solution polymerization is particularly preferable.

 Examples of the radical polymerization initiators include azo compounds, such as 2,2'-azobisisobutyronitrile (AIBN) and 2,2'-azobis-(2,4-dimethylvaleronitrile); and organic peroxides, such as
20 benzoyl peroxide, lauryl peroxide and t-butyl peroxide.

 The solvent for use in the solution polymerization is not specifically restricted provided that it has no reactivity to the monomer components used and is capable of dissolving the resulting polymer. Examples of such

solvents include methanol, ethanol, n-hexane, toluene tetrahydrofuran, 1,4-dioxane, ethyl acetate, n-butyl acetate, acetone, methyl ethyl ketone, methyl isobutyl ketone, 2-heptanone, cyclohexanone, ethylene glycol monomethyl ether, propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, ethyl lactate and γ -butyrolactone.

The above solvents can be used singly or as a mixture of two or more kinds.

When the polymer (A) is prepared by solution polymerization, the polymer solution obtained may be used as it is in the preparation of the positive radiation-sensitive resin composition, or after the polymer (A) is separated from the polymer solution, the polymer may be used in the preparation of the positive radiation-sensitive resin composition.

In the polymerization, a molecular weight modifier such as a mercaptan compound or a halogenated hydrocarbon can be used, when needed.

The molecular weight of the polymer (A) can be controlled by properly selecting polymerization conditions, such as types and amounts of monomers, radical polymerization initiator, molecular weight

modifier and polymerization temperature. The polymer (A) has a weight-average molecular weight (Mw), in terms of polystyrene, of usually 5,000 to 300,000, preferably 7,000 to 200,000.

5 When Mw of the polymer (A) is in the above range, the resin film has sufficient strength and sufficient plating resistance, exhibits excellent alkali solubility after exposure of the polymer, and easily forms a fine pattern.

10 In the present invention, the polymers (A) can be used singly or as a mixture of two or more kinds.

Acid generator (B)

 The radiation-sensitive acid generator (referred to as an "acid generator (B)" hereinafter) for use in the
15 invention is a compound which generates an acid upon exposure. By virtue of an action of the acid generated, the acid-dissociable functional group present in the polymer (A) is dissociated to form an acidic functional group such as a carboxyl group or a phenolic hydroxyl
20 group. As a result, the exposed portion of the resin film formed from the positive radiation-sensitive resin composition comes to have easy solubility in an alkali developing solution, and a positive pattern can be formed.

The acid generator (B) is, for example, an onium salt compound (including thiophenium salt compound), a halogen-containing compound, a diazoketone compound, a sulfone compound, a sulfonic acid compound, a sulfonimide compound or a diazomethane compound. Examples of these compounds are given below.

Examples of the onium salt compounds include iodonium salts, sulfonium salts, phosphonium salts, diazonium salts and pyridinium salts.

Preferred examples of the onium salt compounds include diphenyliodonium trifluoromethanesulfonate, diphenyliodonium p-toluenesulfonate, diphenyliodonium hexafluoroantimonate, diphenyliodonium hexafluorophosphate, diphenyliodonium tetrafluoroborate, triphenylsulfonyl trifluoromethanesulfonate, triphenyl hexafluoroantimonate, triphenylsulfonium hexafluorophosphate, 4-t-butylphenyl·diphenylsulfonium trifluoromethanesulfonate, 4-t-butylphenyl·diphenylsulfonium perfluoro-n-octanesulfonate, 4-t-butylphenyl·diphenylsulfonium pyrenesulfonate, 4-t-butylphenyl·diphenylsulfonium n-dodecylbenzenesulfonate, 4-t-butylphenyl·diphenylsulfonium p-toluenesulfonate, 4-t-butylphenyl·diphenylsulfonium benzenesulfonate and 4,7-

di-n-butoxynaphthyltetrahydrothiophenium
trifluoromethanesulfonate.

Examples of the halogen-containing compounds include
haloalkyl group-containing hydrocarbon compounds and
5 haloalkyl group-containing heterocyclic compounds.

Preferred examples of the halogen-containing
compounds include 1,10-dibromo-n-decane, 1,1-bis(4-
chlorophenyl)-2,2,2-trichloroethane, and
(trichloromethyl)-s-triazine derivatives, such as phenyl-
10 bis(trichloromethyl)-s-triazine, 4-methoxyphenyl-
bis(trichloromethyl)-s-triazine, styryl-
bis(trichloromethyl)-s-triazine and naphthyl-
bis(trichloromethyl)-s-triazine.

Examples of the diazoketone compounds include 1,3-
15 diketo-2-diazo compounds, diazobenzoquinone compounds and
diazonaphthoquinone compounds.

Preferred examples of the diazoketone compounds
include 1,2-naphthoquinonediazido-4-sulfonic esters of
phenols and 1,2-naphthoquinonediazido-5-sulfonic esters
20 of phenols.

Examples of the sulfone compounds include β -
ketosulfone, β -sulfonylsulfone and α -diazo compounds of
these compounds.

Preferred examples of the sulfone compounds include 4-trisphenacylsulfone, mesitylphenacylsulfone and bis(phenylsulfonyl)methane.

Examples of the sulfonic acid compounds include
5 alkylsulfonic esters, haloalkylsulfonic esters, arylsulfonic esters and iminosulfonates.

Preferred examples of the sulfonic acid compounds include benzoin tosylate, pyrogallol tristrifluoromethanesulfonate, o-nitrobenzyl
10 trifluoromethanesulfonate and o-nitrobenzyl p-toluenesulfonate.

Examples of the sulfonimide compounds include N-(trifluoromethylsulfonyloxy)succinimide, N-(trifluoromethylsulfonyloxy)phthalimide, N-
15 (trifluoromethylsulfonyloxy)diphenylmaleimide, N-(trifluoromethylsulfonyloxy)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide, N-(trifluoromethylsulfonyloxy)-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide, N-(trifluoromethylsulfonyloxy)bicyclo[2.2.1]heptan-5,6-oxy-
20 2,3-dicarboxyimide, N-(trifluoromethylsulfonyloxy)naphthylimide, N-(4-methylphenylsulfonyloxy)succinimide, N-(4-methylphenylsulfonyloxy)phthalimide, N-(4-methylphenylsulfonyloxy)diphenylmaleimide, N-(4-

methylphenylsulfonyloxy)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide, N-(4-methylphenylsulfonyloxy)-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide, N-(4-methylphenylsulfonyloxy)bicyclo[2.2.1]heptan-5,6-oxy-2,3-dicarboxyimide, N-(4-methylphenylsulfonyloxy)naphthylimide, N-(2-trifluoromethylphenylsulfonyloxy)succinimide, N-(2-trifluoromethylphenylsulfonyloxy)phthalimide, N-(2-trifluoromethylphenylsulfonyloxy)diphenylmaleimide, N-(2-trifluoromethylphenylsulfonyloxy)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide, N-(2-trifluoromethylphenylsulfonyloxy)-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide, N-(2-trifluoromethylphenylsulfonyloxy)bicyclo[2.2.1]heptan-5,6-oxy-2,3-dicarboxyimide, N-(2-trifluoromethylphenylsulfonyloxy)naphthylimide, N-(4-fluorophenylsulfonyloxy)succinimide, N-(4-fluorophenylsulfonyloxy)-7-oxabicyclo[2.1.1]hept-5-ene-2,3-dicarboxyimide, N-(4-fluorophenylsulfonyloxy)bicyclo[2.1.1]heptan-5,6-oxy-2,3-dicarboxyimide, N-(4-fluorophenylsulfonyloxy)naphthylimide and N-(10-camphorsulfonyloxy)naphthylimide.

Examples of the diazomethane compounds include
bis(trifluoromethylsulfonyl)diazomethane,
bis(cyclohexylsulfonyl)diazomethane,
bis(phenylsulfonyl)diazomethane, bis(p-
5 toluenesulfonyl)diazomethane, methylsulfonyl-p-
toluenesulfonyldiazomethane, cyclohexylsulfonyl-1,1-
dimethylethylsulfonyldiazomethane and bis(1,1-
dimethylethylsulfonyl)diazomethane.

Of the above acid generators (B), 4-t-
10 butylphenyl·diphenylsulfonium trifluoromethanesulfonate,
4-t-butylphenyl·diphenylsulfonium perfluoro-n-
octanesulfonate, 4-t-butylphenyl·diphenylsulfonium
pyrenesulfonate and 4,7-di-n-
butoxynaphthyltetrahydrothiophenium
15 trifluoromethanesulfonate are more preferable, and 4-t-
butylphenyl·diphenylsulfonium trifluoromethanesulfonate
and 4,7-di-n-butoxynaphthyltetrahydrothiophenium
trifluoromethanesulfonate are particularly preferable.

In the present invention, the acid generators (B)
20 can be used singly or as a mixture of two or more kinds.

From the viewpoint of security of sensitivity,
resolution and pattern shape of the resist, the amount of
the acid generator (B) used is in the range of usually
0.1 to 20 parts by weight, preferably 0.3 to 10 parts by

weight, based on 100 parts by weight of the polymer (A).
When the amount of the acid generator (B) used is in the
above range, a resist having excellent sensitivity,
resolution and transparency to radiation is obtained, and
5 a pattern of excellent shape is obtained.

Organic solvent (C)

The positive radiation-sensitive resin composition
of the invention can be diluted with an organic solvent
(C) for the purpose of homogeneously mixing the polymer
10 (A), the acid generator (B), other alkali-soluble resin
(D) described later and additives which are added when
needed.

As the organic solvent, the solvent previously
exemplified with regard to the solution polymerization
15 for preparing the polymer (A) is employable. In addition,
dimethyl sulfoxide, acetonylacetone, isophorone,
propylene carbonate, etc. are also employable. These
organic solvents can be used singly or as a mixture of
two or more kinds.

20 The amount of the organic solvent (C) used can be
controlled by considering a method for applying the
positive radiation-sensitive resin composition, uses of
the composition for producing a plated shaped article,
etc. Although the amount of the organic solvent (C) is

not specifically restricted provided that the composition can be homogeneously mixed, the organic solvent (C) is desirably contained in an amount of preferably 20 to 80 parts by weight, more preferably 30 to 70 parts by weight, based on the total weight 100 parts by weight of the positive radiation-sensitive resin composition. When the amount of the organic solvent (C) is in the above range, the thickness of a resin film formed by applying the composition can be made uniform, and the shape of a desired high bump can be made uniform.

Other alkali-soluble resin

To the positive radiation-sensitive resin composition of the invention, an alkali-soluble resin other than the polymer (A) (referred to as "other alkali-soluble resin (D)" hereinafter) can be added on certain occasions.

The other alkali-soluble resin (D) is a resin which has one or more functional groups showing affinity for an alkali developing solution, e.g., acidic functional groups such as a phenolic hydroxyl group and a carboxyl group, and is soluble in an alkali developing solution.

By adding such an alkali-soluble resin, control of solubility speed of a resin film formed from the positive radiation-sensitive resin composition in an alkali

developing solution can be made easier, and therefore, developability can be further enhanced.

The other alkali-soluble resin (D) is not specifically restricted as long as it is soluble in an alkali developing solution. Examples of the resins (D) include addition polymerization type resins obtained by polymerizing at least one monomer having an acidic functional group, such as o-hydroxystyrene, m-hydroxystyrene, p-hydroxystyrene, p-isopropenylphenol, p-vinylbenzoic acid, p-carboxymethylstyrene, p-carboxymethoxystyrene, acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, mesaconic acid and cinnamic acid; and polycondensation type resins having an acidic functional group, such as a novolak resin.

The addition polymerization type alkali-soluble resin may be constituted of only recurring units formed by cleavage of polymerizable unsaturated bonds of the monomer having an acidic functional group, but the resin can further contain one or more kinds of other recurring units as long as the resulting resin is soluble in an alkali developing solution.

Examples of other recurring units include those of styrene, α -methylstyrene, o-vinyltoluene, m-vinyltoluene,

p-vinyltoluene, maleic anhydride, acrylonitrile, methacrylonitrile, crotonitrile, maleinitrile, fumaronitrile, mesaconitrile, citraconitrile, itaconitrile, acrylamide, methacrylamide, crotonamide, 5 maleinamide, fumaramide, mesaconamide, citraconamide, itaconamide, 2-vinylpyridine, 3-vinylpyridine, 4-vinylpyridine, N-vinylaniline, N-vinyl- ϵ -caprolactam, N-vinylpyrrolidone and N-vinylimidazole.

The addition polymerization type alkali-soluble 10 resin is particularly preferably poly(p-hydroxystyrene) or a copolymer of p-isopropenylphenol from the viewpoints that radiation transmittance of the resulting resin film is high and dry etching resistance thereof is excellent.

The addition polymerization type alkali-soluble 15 resin has a weight-average molecular weight (M_w), in terms of polystyrene, of usually 1,000 to 200,000, preferably 5,000 to 50,000.

The polycondensation type alkali-soluble resin may be constituted of only condensation recurring units 20 having an acidic functional group, but the resin can further contain other condensation recurring units as long as the resulting resin is soluble in an alkali developing solution.

Such a polycondensation type resin can be prepared by, for example, (co)polycondensing one or more phenols and one or more aldehydes, and in certain cases, together with a polycondensation component capable of forming
5 other condensation recurring units, in a water medium or a mixed medium of water and a hydrophilic solvent in the presence of an acid catalyst or a basic catalyst.

Examples of the phenols include o-cresol, m-cresol, p-cresol, 2,3-xyleneol, 2,4-xyleneol, 2,5-xyleneol, 3,4-
10 xyleneol, 3,5-xyleneol, 2,3,5-trimethylphenol and 3,4,5-trimethylphenol. Examples of the aldehydes include formaldehyde, trioxane, paraformaldehyde, benzaldehyde, acetaldehyde, propylaldehyde and phenylacetaldehyde.

The polycondensation type alkali-soluble resin has a
15 weight-average molecular weight (Mw), in terms of polystyrene, of usually 1,000 to 100,000, preferably 2,000 to 50,000.

The above-mentioned other alkali-soluble resins can be used singly or as a mixture of two or more kinds. The
20 amount of the other alkali-soluble resin used is usually not more than 200 parts by weight based on 100 parts by weight of the polymer (A).

Acid diffusion controller

In order to control diffusion of an acid generated from the acid generator (B) into the resin film and thereby inhibit undesirable chemical reaction in the unexposed portion, it is preferable to add an acid diffusion controller to the positive radiation-sensitive resin composition of the invention. By the use of the acid diffusion controller, storage stability of the composition is improved, and resolution of the resist can be increased. In addition, change of line width of the pattern attributable to variation of the post-exposure delay time between exposure and PEB can be inhibited, and the process stability becomes very excellent.

The acid diffusion controller is preferably a nitrogen-containing organic compound whose basicity is not changed by exposure or heating in the production process of a plated shaped article.

Examples of the nitrogen-containing organic compounds include n-hexylamine, n-heptylamine, n-octylamine, n-nonylamine, ethylenediamine, N,N,N',N'-tetramethylethylenediamine, tetamethylenediamine, hexamethylenediamine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl ether, 4,4'-diaminobenzophenone, 4,4'-diaminodiphenylamine, formamide, N-methylformamide, N,N-

dimethylformamide, acetamide, N-methylacetamide, N,N-dimethylacetamide, propionamide, benzamide, pyrrolidone, N-methylpyrrolidone, methylurea, 1,1-dimethylurea, 1,3-dimethylurea, 1,1,3,3-tetramethylurea, 1,3-diphenylurea, 5 imidazole, benzimidazole, 4-methylimidazole, 8-oxyquinoline, acridine, purine, pyrrolidine, piperidine, 2,4,6-tri(2-pyridyl)-s-triazine, morpholine, 4-methylmorpholine, piperazine, 1,4-dimethylpiperazine and 1,4-diazabicyclo[2.2.2]octane. Of these nitrogen- 10 containing organic compounds, 2,4,6-tri(2-pyridyl)-s-triazine is particularly preferable.

The acid diffusion controllers can be used singly or as a mixture of two or more kinds.

The amount of the acid diffusion controller used is 15 usually not more than 15 parts by weight, preferably 0.001 to 10 parts by weight, more preferably 0.005 to 5 parts by weight, based on 100 parts by weight of the polymer (A). When the amount of the acid diffusion controller is in the above range, a resist excellent in 20 sensitivity, developability, pattern shape and dimensional fidelity can be obtained.

Surface active agent

In order to improve coating property, developability, etc., a surface active agent can be added to the positive radiation-sensitive resin composition of the invention.

5 Examples of the surface active agents include polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene n-octylphenol ether, polyoxyethylene n-nonylphenol ether, polyethylene glycol dilaurate and polyethylene glycol
10 distearate.

The above surface active agents can be used singly or as a mixture of two or more kinds. The amount of the surface active agent used is usually not more than 2 parts by weight based on 100 parts by weight of the
15 polymer (A).

Other additives

As other additives which can be added to the positive radiation-sensitive resin composition of the invention, there can be mentioned, for example,
20 ultraviolet light absorber, sensitizier, dispersant, plasticizer, thermal polymerization inhibitor for enhancing storage stability, and antioxidant. Above all, the ultraviolet light absorber is useful because it has a function of inhibiting photo reaction caused by entering

of scattered light into the unexposed portion in the exposure step. Such an ultraviolet light absorber is preferably a compound having a high absorptivity coefficient in the wavelength region of ultraviolet light used for the exposure. Further, an organic pigment is also employable for the same purpose.

The positive radiation-sensitive resin composition of the invention is excellent in heat resistance in the PEB step, wettability of the resin film by a developing solution, and adhesion of the resin film to a substrate. Particularly, high heat resistance of the resin composition in the PEB step is very important for the contribution to resolution of a resist, so that the resin composition can be preferably used for producing a plated shaped article such as a bump or a wiring of an integrated circuit device.

The process for producing a plated shaped article according to the invention comprises:

- (1) a step of forming a resin film composed of the above-described positive radiation-sensitive resin composition on a wafer having a barrier metal layer,
- (2) a step of exposing the resin film and then developing the resin film to form a pattern,

(3) a step of depositing an electrode material by electroplating using the pattern as a mold, and

(4) a step of stripping the remaining resin film and then removing the barrier metal by etching.

5 The resin film formed in the step (1) can be obtained by applying the resin composition of the invention onto a wafer and drying the composition. Further, the resin film can be obtained also by the use of the below-described transfer film of the invention,
10 and specifically, the resin film can be obtained by transferring a resin film onto a wafer from the transfer film.

 The transfer film of the invention has a resin film composed of the positive radiation-sensitive resin
15 composition on a support film. Such a transfer film can be prepared by applying the positive radiation-sensitive resin composition onto a support film and drying the composition. Examples of methods to apply the composition include spin coating, roll coating, screen
20 printing and applicator method. The material of the support film is not specifically restricted as long as the material has a strength capable of withstanding preparation and uses of a transfer film.

In the transfer film employable as the present invention, the thickness of the resin film is in the range of 20 to 200 μm .

By peeling the support film from the transfer film
5 of the invention, a positive radiation-sensitive resin film can be obtained. The resin film thus obtained can be used for producing a plated shaped article, similarly to the case of using the composition of the invention.

10

EXAMPLES

The present invention is further described with reference to the following examples, but it should be construed that the invention is in no way limited to those examples. In the following examples, the terms
15 "part(s)" and "%" mean "part(s) by weight" and "% by weight", respectively, unless otherwise noted.

Synthesis of polymer (A)

Synthesis Example 1

20 g of p-hydroxyphenyl methacrylamide, 20 g of p-
20 isopropenylphenol, 20 g of 2-hydroxyethyl acrylate, 20 g of isobornyl acrylate and 30 g of 2-benzyl-2-propyl methacrylate were mixed with 150 g of ethyl lactate, and the mixture was stirred at 50°C to give a homogeneous solution. After a nitrogen gas was bubbled through the

solution for 30 minutes, 4 g of AIBN was added. With continuing bubbling of a nitrogen gas and maintaining the reaction temperature at 70°C, polymerization was carried out for 7 hours. After the polymerization was completed, 5 the reaction solution was mixed with a large amount of hexane to solidify the resulting polymer. Subsequently, the polymer was redissolved in tetrahydrofuran and then solidified by the use of hexane again. These operations were repeated several times to remove the unreacted 10 monomers, and the resulting polymer was dried at 50°C under reduced pressure to obtain a white polymer A1.

Synthesis Examples 2 to 10

Copolymers A2 to A10 were synthesized in the same 15 manner as in the synthesis of the copolymer A1 of Synthesis Example 1, except that the types and the amounts of the compounds were changed in accordance with compositions of Table 1. Further, copolymers A11 to A25 were synthesized in the same manner as in the synthesis 20 of the copolymer A1 of Synthesis Example 1, except that the solvent used was changed to propylene glycol monomethyl ether acetate.

Synthesis of polymer for comparison

Synthesis Example 11

30 g of p-isopropenylphenol, 20 g of 2-hydroxyethyl acrylate and 50 g of 2-benzyl-2-propyl acrylate were mixed with 150 g of ethyl lactate to give a homogeneous solution. After a nitrogen gas was bubbled through the solution for 30 minutes, 4 g of AIBN was added. With continuing bubbling of a nitrogen gas and maintaining the reaction temperature at 70°C, polymerization was carried out for 7 hours. After the polymerization was completed, the reaction solution was mixed with a large amount of hexane to solidify the resulting polymer. Subsequently, the polymer was redissolved in tetrahydrofuran and then solidified by the use of hexane again. These operations were repeated several times to remove the unreacted monomers, and the resulting polymer was dried at 50°C under reduced pressure to obtain a white polymer R1.

Synthesis Examples 12 and 13

Copolymers R2 and R3 were synthesized in the same manner as in the synthesis of the copolymer R1 of Synthesis Example 11, except that the types and the amounts of the compounds were changed in accordance with compositions of Table 1.

Synthesis of polymer (D)Synthesis Example 14

30 g of p-isopropenylphenol, 30 g of 2-hydroxyethyl acrylate, 35 g of n-butyl acrylate, 5 g of 2-methoxyethyl acrylate and 1 g of n-hexyl 1,6-dimethacrylate were mixed with 150 g of propylene glycol monomethyl ether acetate to give a homogeneous solution. After a nitrogen gas was bubbled through the solution for 30 minutes, 4 g of AIBN was added. With continuing bubbling of a nitrogen gas and maintaining the reaction temperature at 80°C, polymerization was carried out for 6 hours. After the polymerization was completed, the reaction solution was mixed with a large amount of hexane to solidify the resulting polymer. Subsequently, the polymer was redissolved in tetrahydrofuran and then solidified by the use of hexane again. These operations were repeated several times to remove the unreacted monomers, and the resulting polymer was dried at 50°C under reduced pressure to obtain a white polymer D1.

20

Synthesis Example 15

50 g of 2-hydroxyethyl methacrylate, 40 g of n-butyl acrylate and 10 g of 2-methacryloyloxyethyl hexahydrophthalate were mixed with 150 g of ethyl lactate

to give a homogeneous solution. After a nitrogen gas was bubbled through the solution for 30 minutes, 4 g of AIBN was added. With continuing bubbling of a nitrogen gas and maintaining the reaction temperature at 80°C, polymerization was carried out for 6 hours. After the polymerization was completed, the reaction solution was mixed with a large amount of hexane to solidify the resulting polymer. Subsequently, the polymer was redissolved in tetrahydrofuran and then solidified by the use of hexane again. These operations were repeated several times to remove the unreacted monomers, and the resulting polymer was dried at 50°C under reduced pressure to obtain a white polymer D2. The polymer was dissolved in ethyl lactate to give a solution having a concentration of 50% by weight, and this solution was used.

Example 1

Preparation of resin composition

In 150 parts by weight of ethyl lactate (organic solvent (C1)), 100 parts by weight of the polymer (A1), 3 parts by weight of 4,7-di-n-butoxynaphthyltetrahydrothiophenium trifluoromethanesulfonate (acid generator (B)) and 20

parts by weight of the polymer (D1) were dissolved, and the resulting solution was filtered through a Teflon (R) membrane filter having a pore diameter of 3 μm to prepare a resin composition.

5 Preparation of gold sputtered substrate

On a silicon wafer substrate having a diameter of 4 inches, chromium was sputtered in a thickness of about 500 Å, and then gold was further sputtered thereon in a thickness of 1,000 Å to form a conductive layer. This
10 substrate provided with the conductive layer is referred to as a "gold sputtered substrate" hereinafter.

Formation of pattern

The gold sputtered substrate was coated with the resin composition by means of a spin coater and then
15 heated on a hot plate at 120°C for 5 minutes to form a resin film having a thickness of 25 μm . Subsequently, the resin film was irradiated with ultraviolet light of 300 to 1500 mJ/cm² using an extra-high pressure mercury lamp (OSRAM HBO, output: 1,000 W) through a pattern mask.
20 The quantity of light for exposure was confirmed by an illuminance meter (UV-M10 (illuminance meter, manufactured by ORC Manufacturing Co., Ltd.) to which a probe UV-35 (receptor) had been connected). After the exposure, PEB was carried out on a hot plate at 100°C for

5 minutes. Subsequently, the resin film was immersed in a 2.38 wt% tetramethylammonium hydroxide aqueous solution at room temperature for 1 to 5 minutes to develop the resin film, then washed with running water and subjected to nitrogen blowing to form a pattern. This substrate provided with the pattern is referred to as a "patterning substrate (A)" hereinafter.

Formation of plated shaped article

The patterning substrate (A) was subjected to ashing treatment with oxygen plasma (output: 100 W, oxygen flow rate: 100 ml, treating time: 1 minute) as pretreatment for electroplating, to make the patterning substrate hydrophilic. Subsequently, the substrate was immersed in 1 liter of a gold cyanide plating solution (available from Electroplating Engineers of Japan Ltd., trade name: Temperex 401) and subjected to electroplating for about 60 minutes under the conditions of a plating bath temperature of 42°C and a current density of 0.6 A/dm² to form a plated shaped article for a bump having a thickness of 15 to 18 μm. Then, the substrate was washed with running water and blown by a nitrogen gas to dry it. Thereafter, the substrate was immersed in a mixed solution of dimethyl sulfoxide and N,N-dimethylformamide (weight ratio = 50:50) at room temperature for 5 minutes

to strip the resin film portion, and then a portion of the conductive layer on the substrate other than the region where the plated shaped article had been formed was removed by wet etching to obtain a substrate having a plated shaped article. This substrate having the plated shaped article is referred to as a "plated substrate (A)" hereinafter.

Evaluation

(1) Sensitivity

10 A quantity of light for exposure, by which a dimension of a bottom of a removed pattern becomes 30 μm when a pattern of 40 μm pitch in a mask design dimension (removed pattern of 30 μm width/remaining pattern of 10 μm width) is formed on a gold sputtered substrate, was
15 taken as an optimum quantity of light for exposure, and the sensitivity was evaluated by this optimum quantity of light for exposure.

(2) Resolution

20 Two kinds of patterns of 40 μm pitch in a mask design dimension (removed pattern of 30 μm width/remaining pattern of 10 μm width, removed pattern of 32 μm width/remaining pattern of 8 μm width) were formed on substrates separately to prepare two patterning substrates (A). These two patterning substrates (A) were

observed by a light microscope and a scanning electron microscope and evaluated based on the following criteria.

AA: The removed pattern of 32 μm width/remaining pattern of 8 μm width could be resolved.

5 BB: Although the removed pattern of 30 μm width/remaining pattern of 10 μm width could be resolved, the removed pattern of 32 μm width/remaining pattern of 8 μm width could not be resolved.

CC: The pattern of 40 μm pitch could not be resolved
10 or could not be resolved with good reproducibility.

(3) Crack resistance

Using the patterning substrate (A), a plated shaped article for a bump was formed in the same manner as in the formation of the aforesaid plated shaped article.
15 Then, the substrate was washed with running water and blown by a nitrogen gas to dry it. The resulting substrate (i.e., substrate from which the resin film portion had not been stripped) was allowed to stand in a clean room kept at room temperature (23°C) and a humidity
20 of about 45%. After a lapse of 3 hours and a lapse of 24 hours, the substrate surface was observed by a light microscope, and the substrate was evaluated based on the following criteria. The term "remaining pattern" used herein corresponds to a resist pattern.

AA: Even after 24 hours, no crack occurs in the remaining pattern.

BB: After 3 hours, no crack occurs in the remaining pattern, but after 24 hours, a crack occurs in the
5 remaining pattern.

CC: After 3 hours, a crack occurs in the remaining pattern.

(4) Dimensional fidelity of pattern

The patterning substrate (A) provided with a pattern
10 of 40 μm pitch in a mask dimension (removed pattern of 30
 μm width/remaining pattern of 10 μm width) was observed
by a light microscope and a scanning electron microscope,
and a top dimension (Wt) and a bottom dimension (Wb) of
the removed pattern were measured to evaluate the
15 dimensional fidelity of the pattern to the mask dimension
(30 μm).

(5) Shape (A) of plated portion

The patterning substrate (A) provided with a pattern
of 40 μm pitch in a mask dimension (removed pattern of 30
20 μm width/remaining pattern of 10 μm width) was observed
by a light microscope and a scanning electron microscope,
and the substrate was evaluated based on the following
criteria.

AA: The shape of the plated portion has been transferred from the shape of the pattern formed from the resin film with fidelity, and any abnormal nodular protrusion is not observed.

5 BB: The shape of the plated portion has not been transferred from the shape of the pattern formed from the resin film with fidelity, and an abnormal nodular protrusion is observed.

(6) Shape (B) of plated portion

10 The patterning substrate (A) provided with a pattern of 40 μm pitch in a mask dimension (removed pattern of 30 μm width/remaining pattern of 10 μm width) was observed by a light microscope and a scanning electron microscope, and the substrate was evaluated based on the following
15 criteria.

AA: The shape of the bottom of the plated portion has been transferred from the shape of the pattern formed from the resin film with fidelity, and traces of introduction of the plating solution between the bottom
20 of the pattern and the surface of the substrate are not observed.

BB: The shape of the bottom of the plated portion has not been transferred from the shape of the pattern formed from the resin film with fidelity, and traces of

introduction of the plating solution between the bottom of the pattern and the surface of the substrate are observed.

(7) Dimensional fidelity of plated portion

5 The plated substrate (A) obtained by forming a plated shaped article on the patterning substrate (A) provided with a pattern of 40 μm pitch in a mask dimension (removed pattern of 30 μm width/remaining pattern of 10 μm width) was observed by a light
10 microscope and a scanning electron microscope, and a top dimension (Wt) and a bottom dimension (Wb) of the plated portion were measured to evaluate the dimensional fidelity of plated portion to the mask dimension (30 μm).

The evaluation results are set forth in Table 3.

15

Example 2

A resin composition was prepared in the same manner as in Example 1, except that the components and the amounts thereof were changed to those shown in Example 2
20 of Table 2. Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

Example 3

A resin composition was prepared in the same manner as in Example 1, except that the components and the amounts thereof were changed to those shown in Example 3 of Table 2, and 2,4,6-tri(2-pyridyl)-s-triazine (acid diffusion controller (E)) was added in an amount of 0.05 part by weight based on 100 parts by weight of the polymer (A1). Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

Example 4

A resin composition was prepared in the same manner as in Example 3, except that the components and the amounts thereof were changed to those shown in Example 4 of Table 2. Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

Example 5

A resin composition was prepared in the same manner as in Example 3, except that the components and the

amounts thereof were changed to those shown in Example 5 of Table 2, and the polymer (A2) was used instead of the polymer (A1). Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

Example 6

A resin composition was prepared in the same manner as in Example 3, except that the components and the amounts thereof were changed to those shown in Example 6 of Table 2, and polyvinyl methyl ether (polymer (D3), Mw: 50,000, available from Tokyo Kasei Kogyo Co., Ltd.) was used instead of the polymer (D1). Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

The polymer (D3) was used as a solution having a concentration of 50% by weight, which had been obtained by subjecting an ethanol solution of the polymer having a concentration of 50% by weight to solvent replacement with ethyl lactate by means of a rotary evaporator.

Example 7

A resin composition was prepared in the same manner as in Example 1, except that the components and the amounts thereof were changed to those shown in Example 7 of Table 2, and the polymer (A2) was used instead of the polymer (A1). Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

10

Example 8

A resin composition was prepared in the same manner as in Example 1, except that the components and the amounts thereof were changed to those shown in Example 8 of Table 2, and the polymer (A3) was used instead of the polymer (A1). Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

20

Example 9

A resin composition was prepared in the same manner as in Example 1, except that the components and the amounts thereof were changed to those shown in Example 9

of Table 2, and the polymer (A4) was used instead of the polymer (A1). Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation
5 results are set forth in Table 3.

Example 10

A resin composition was prepared in the same manner as in Example 1, except that the components and the
10 amounts thereof were changed to those shown in Example 10 of Table 2, and the polymer (A5) was used instead of the polymer (A1). Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation
15 results are set forth in Table 3.

Example 11

A resin composition was prepared in the same manner as in Example 1, except that the components and the
20 amounts thereof were changed to those shown in Example 11 of Table 2, and the polymer (A6) was used instead of the polymer (A1). Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out

in the same manner as in Example 1. The evaluation results are set forth in Table 3.

Example 12

5 A resin composition was prepared in the same manner as in Example 1, except that the components and the amounts thereof were changed to those shown in Example 12 of Table 2, and the polymer (A7) was used instead of the polymer (A1). Then, formation of a pattern, formation of
10 a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

Example 13

15 A resin composition was prepared in the same manner as in Example 1, except that the components and the amounts thereof were changed to those shown in Example 13 of Table 2, and the polymer (A8) was used instead of the polymer (A1). Then, formation of a pattern, formation of
20 a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

Example 14

A resin composition was prepared in the same manner as in Example 1, except that the components and the amounts thereof were changed to those shown in Example 14 of Table 2, and the polymer (A9) was used instead of the polymer (A1). Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

10

Example 15

A resin composition was prepared in the same manner as in Example 1, except that the components and the amounts thereof were changed to those shown in Example 15 of Table 2, and the polymer (A10) was used instead of the polymer (A1). Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

20

Example 16

In 150 parts by weight of propylene glycol monomethyl ether acetate (organic solvent (C2)), 100 parts by weight of the polymer (A11) and 3 parts by

weight of 4,7-di-n-butoxynaphthyltetrahydrothiophenium trifluoromethanesulfonate (acid generator (B)) were dissolved, and the resulting solution was filtered through a Teflon (R) membrane filter having a pore diameter of 3 μ m to prepare a resin composition. Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

10

Example 17

A resin composition was prepared in the same manner as in Example 16, except that the components and the amounts thereof were changed to those shown in Example 17 of Table 2, and 2,4,6-tri(2-pyridyl)-s-triazine (acid diffusion controller (E)) was newly added in an amount of 0.05 part by weight based on 100 parts by weight of the polymer (A1). Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

20

Example 18

A resin composition was prepared in the same manner as in Example 17, except that the components and the amounts thereof were changed to those shown in Example 18 of Table 2. Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

10 Example 19

A resin composition was prepared in the same manner as in Example 17, except that the components and the amounts thereof were changed to those shown in Example 19 of Table 2. Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

Example 20

20 A resin composition was prepared in the same manner as in Example 17, except that the components and the amounts thereof were changed to those shown in Example 20 of Table 2. Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in

the same manner as in Example 1. The evaluation results are set forth in Table 3.

Example 21

5 A resin composition was prepared in the same manner as in Example 17, except that the components and the amounts thereof were changed to those shown in Example 21 of Table 2. Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in
10 the same manner as in Example 1. The evaluation results are set forth in Table 3.

Example 22

15 A resin composition was prepared in the same manner as in Example 17, except that the components and the amounts thereof were changed to those shown in Example 22 of Table 2. Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in
20 the same manner as in Example 1. The evaluation results are set forth in Table 3.

Example 23

 A resin composition was prepared in the same manner as in Example 17, except that the components and the

amounts thereof were changed to those shown in Example 23 of Table 2. Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results
5 are set forth in Table 3.

Example 24

A resin composition was prepared in the same manner as in Example 17, except that the components and the
10 amounts thereof were changed to those shown in Example 24 of Table 2. Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

15

Example 25

A resin composition was prepared in the same manner as in Example 17, except that the components and the amounts thereof were changed to those shown in Example 25
20 of Table 2. Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

Example 26

A resin composition was prepared in the same manner as in Example 17, except that the components and the amounts thereof were changed to those shown in Example 26 of Table 2. Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

10 Comparative Examples 1 to 3

Resin compositions were prepared in the same manner as in Example 1, except that the components and the amounts thereof were changed to those shown in Comparative Examples 1 to 3 of Table 2, and the polymer (R1) was used instead of the polymer (A1). Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

20

Comparative Example 4

A resin composition was prepared in the same manner as in Example 1, except that the components and the amounts thereof were changed to those shown in

Comparative Example 4 of Table 2, and the polymer (R2) was used instead of the polymer (A1). Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in
5 Example 1. The evaluation results are set forth in Table 3.

Comparative Example 5

A resin composition was prepared in the same manner
10 as in Example 1, except that the components and the amounts thereof were changed to those shown in Comparative Example 5 of Table 2, and the polymer (R3) was used instead of the polymer (A1). Then, formation of a pattern, formation of a plated shaped article and
15 evaluations were carried out in the same manner as in Example 1. The evaluation results are set forth in Table 3.

Example 27

20 Preparation of resin composition

In 100 parts by weight of propylene glycol monomethyl ether acetate (organic solvent (C2)), 100 parts by weight of the polymer (A21) and 3 parts by weight of 4,7-di-n-butoxynaphthyltetrahydrothiophenium

trifluoromethanesulfonate (acid generator (B)) were dissolved, and the resulting solution was filtered through a Teflon (R) membrane filter having a pore diameter of 3 μm to prepare a resin composition.

5 Preparation of copper sputtered substrate

On a silicon wafer substrate having a diameter of 4 inches, TiW was sputtered in a thickness of about 1,000 Å, and then copper was further sputtered thereon in a thickness of 3,000 Å to form a conductive layer. This
10 substrate provided with the conductive layer is referred to as a "copper sputtered substrate" hereinafter.

Formation of pattern

The copper sputtered substrate was coated with the resin composition by means of a spin coater. Thereafter,
15 the copper sputtered substrate was heated on a hot plate at 130°C for 10 minutes to form a resin film having a thickness of 80 μm . Subsequently, the resin film was irradiated with ultraviolet light of 500 to 2000 mJ/cm^2 using an extra-high pressure mercury lamp (OSRAM HBO,
20 output: 1,000 W) through a pattern mask of a given shape. The quantity of light for exposure was confirmed by an illuminance meter (UV-M10 (illuminance meter, manufactured by ORC Manufacturing Co., Ltd.) to which a probe UV-35 (receptor) had been connected). After the

exposure, PEB was carried out on a hot plate at 90°C for 5 minutes. Subsequently, the resin film was immersed in a 2.38 wt% tetramethylammonium hydroxide aqueous solution at room temperature for 1 to 5 minutes to develop the resin film, then washed with running water and subjected to nitrogen blowing to form a pattern. This substrate provided with the pattern is referred to as a "patterning substrate (B)" hereinafter.

Formation of plated shaped article

10 The patterning substrate (B) was subjected to ashing treatment with oxygen plasma (output: 100 W, oxygen flow rate: 100 ml, treating time: 1 minute) as pretreatment for electroplating, to make the patterning substrate hydrophilic. Subsequently, the substrate was immersed in 15 1 liter of a copper plating solution (available from Electroplating Engineers of Japan Ltd., trade name: Microfab Cu200) and subjected to electroplating for about 90 minutes under the conditions of a plating bath temperature of 25°C and a current density of 3.0 A/dm² to 20 form a plated shaped article for a bump having a thickness of about 60 µm. Then, the substrate was washed with running water and blown by a nitrogen gas to dry it. Thereafter, the substrate was immersed in N-methylpyrrolidone at room temperature for 5 minutes to

strip the resin film portion, and then a portion of the conductive layer on the substrate other than the region where the plated shaped article had been formed was removed by wet etching to obtain a substrate having a plated shaped article. This substrate having the plated shaped article is referred to as a "plated substrate (B)" hereinafter.

Evaluation

(1) Sensitivity

10 A quantity of light for exposure, by which a dimension of a bottom of a removed pattern becomes 75 μm when a square pattern of 75 $\mu\text{m} \times 75 \mu\text{m}$ in a mask design dimension is formed on a copper sputtered substrate, was taken as an optimum quantity of light for exposure, and
15 the sensitivity was evaluated by this optimum quantity of light for exposure. A case where the quantity of light for exposure was not less than 3,000 mJ/cm^2 was evaluated as "BB", and the subsequent evaluations were discontinued.

(2) Resolution

20 The patterning substrate (B) provided with a square pattern of 50 $\mu\text{m} \times 50 \mu\text{m}$ in a mask design dimension was observed by a scanning electron microscope, and the resolution was evaluated by the resolved image of the square pattern. A case where the pattern was resolved

without a residue of a resist and the resolved image had a sidewall angle of 80 to 90° was evaluated as "AA", and a case other than this case was evaluated as "BB".

(3) Abnormality of pattern shape

5 The patterning substrate (B) provided with a square pattern of 75 μm \times 75 μm in a mask design dimension was observed by a scanning electron microscope to evaluate abnormality of pattern shape. The evaluation was carried out using 5 patterns, that is, a square pattern of 75 μm
10 \times 75 μm present near the center of the substrate as a reference, two patterns each of which is present at a distance of about 2 cm from the reference pattern in the direction of each end of the substrate and two patterns each of which is present at a distance of about 4 cm. A
15 case where the sidewall angles of all the patterns were the same as one another was evaluated as "AA", and a case where at least one of them was different was evaluated as "BB".

(4) Wettability by plating solution

20 The plated substrate (B) obtained by plating the patterning substrate (B) provided with a square pattern of 75 μm \times 75 μm in a mask design dimension was observed by a light microscope to evaluate wettability by a plating solution. The evaluation was carried out based

on the criteria that the surface of the patterning substrate (B) has affinity for a plating solution and no plating defect occurs because air bubbles inside the pattern are completely removed. A case where any plating defect was not present at all in the plated substrate (B) or plating defects were present in patterns of less than 5% only based on 7000 patterns observed was evaluated as "AA", and a case where plating defects were present in patterns of not less than 5% based on 7000 patterns observed was evaluated as "BB".

(5) Plating solution resistance

The plated substrate (B) obtained by plating the patterning substrate (B) provided with a square pattern of $75\ \mu\text{m} \times 75\ \mu\text{m}$ in a mask design dimension was observed by a light microscope to evaluate plating resistance. The evaluation was carried out based on the criteria that the shape of the plated portion after stripping has been transferred from the shape of the resist pattern, that is, the bump width is not more than 103% of the resist pattern and deposition does not occur at the resist opening because the plating solution does not come out from the opening. A case where these two requirements were satisfied was evaluated as "AA", and a case where

these two requirements were not satisfied was evaluated as "BB".

The evaluation results are set forth in Table 4.

5 Example 28

 A resin composition was prepared in the same manner as in Example 27, except that the components and the amounts thereof were changed to those shown in Example 28 of Table 2, and 4,4'-[1-[4-[2-(4-hydroxyphenyl)-2-propyl]phenyl]ethylidene]bisphenol (additive (F),
10 available from Sanbo Chemical Co., Ltd.) was newly added in an amount of 10 parts by weight based on 90 parts by weight of the polymer (A21). Then, formation of a pattern, formation of a plated shaped article and
15 evaluations were carried out in the same manner as in Example 27. The evaluation results are set forth in Table 4.

Example 29

20 A resin composition was prepared in the same manner as in Example 28, except that the components and the amounts thereof were changed to those shown in Example 29 of Table 2. Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in

the same manner as in Example 27. The evaluation results are set forth in Table 4.

Example 30

5 A resin composition was prepared in the same manner as in Example 28, except that the components and the amounts thereof were changed to those shown in Example 30 of Table 2. Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in
10 the same manner as in Example 27. The evaluation results are set forth in Table 4.

Example 31

15 A resin composition was prepared in the same manner as in Example 28, except that the components and the amounts thereof were changed to those shown in Example 31 of Table 2. Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in
the same manner as in Example 27. The evaluation results
20 are set forth in Table 4.

Example 32

A resin composition was prepared in the same manner as in Example 28, except that the components and the

amounts thereof were changed to those shown in Example 32 of Table 2. Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 27. The evaluation results
5 are set forth in Table 4.

Example 33

A resin composition was prepared in the same manner as in Example 28, except that the components and the
10 amounts thereof were changed to those shown in Example 33 of Table 2. Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in Example 27. The evaluation results are set forth in Table 4.

15

Comparative Example 6

A resin composition was prepared in the same manner as in Example 27, except that the components and the amounts thereof were changed to those shown in
20 Comparative Example 6 of Table 2, and the polymer (R1) was used instead of the polymer (A1). Then, formation of a pattern, formation of a plated shaped article and evaluations were carried out in the same manner as in

Example 27. The evaluation results are set forth in
Table 4.

Table 1

Copolymer	Component											
	a	b	c	d	e	f	g	h	i	i'	j	j'
A1	20			20		20	10			30		
A2	15			20		20				45		
A3	10			20		20			50			
A4	5			20		20			55			
A5	20			20		30				30		
A6	20			30		20			30			
A7		20		20		10			50			
A8		15		20		25			40			
A9		10		20		30			40			
A10	20				5	20				55		
A11			40	5		5		20			30	
A12			30	5		10		25			30	
A13			30	10		5		25			30	
A14			40	5		5	20				30	
A15			40	5		5		20				30
A16	10		30	5				25			30	
A17	10		30	10				20			30	
A18	10		20	10				30			30	
A19	10		30	5			25				30	
A20	10		30	5				25				30
A21	10			30					60			
A22	10			40					50			
A23	10			30		5			55			
A24	10			30		10			50			
A25	20			30		10			40			
R1				30		20			50			
R2				20	5	25			50			
R3				10	10	20	10		50			

Table 1 (continued)

- a: p-hydroxyphenyl methacrylamide
- b: 3,5-dimethyl-4-hydroxybenzyl acrylate
- c: 4-hydroxyphenyl methacrylate
- 5 d: p-isopropenylphenol
- e: methacrylic acid
- f: 2-hydroxyethyl acrylate
- g: isobornyl acrylate
- h: benzyl acrylate
- 10 i: 2-benzyl-2-propyl acrylate
- i': 2-benzyl-2-propyl methacrylate
- j: t-butyl acrylate
- j': t-butyl methacrylate

Table 2

	Polymer (A) (part(s))	Polymer (D) (part(s))	Acid generator (B) (part(s))	Acid diffusion controller (part(s))	Additive (part(s))	Organic solvent (part(s))
Ex. 1	A1(100)	D1(20)	B(3)			C1(150)
Ex. 2	A1(100)	D1(30)	B(3)			C1(150)
Ex. 3	A1(100)	D1(20)	B(3)	E1(0.05)		C1(150)
Ex. 4	A1(100)	D1(20)	B(3)	E1(0.10)		C1(150)
Ex. 5	A1(100)	D2(20)	B(3)	E1(0.05)	-	C1(150)
Ex. 6	A1(100)	D3(20)	B(3)	E1(0.05)	-	C1(150)
Ex. 7	A2(100)	D1(20)	B(3)	-	-	C1(150)
Ex. 8	A3(100)	D1(20)	B(3)	-	-	C1(150)
Ex. 9	A4(100)	D1(20)	B(3)	-	-	C1(150)
Ex. 10	A5(100)	D1(20)	B(3)	-	-	C1(150)
Ex. 11	A6(100)	D1(20)	B(3)	-	-	C1(150)
Ex. 12	A7(100)	D1(20)	B(3)	-	-	C1(150)
Ex. 13	A8(100)	D1(20)	B(3)	-	-	C1(150)
Ex. 14	A9(100)	D1(20)	B(3)	-	-	C1(150)
Ex. 15	A10(100)	D1(20)	B(3)	-	-	C1(150)
Ex. 16	A11(100)	-	B(3)	-	-	C2(150)
Ex. 17	A11(100)	-	B(3)	E(0.05)	-	C2(150)
Ex. 18	A12(100)	-	B(3)	E(0.05)	-	C2(150)
Ex. 19	A13(100)	-	B(3)	E(0.05)	-	C2(150)

Table 2 (continued)

	Polymer (A) (part(s))	Polymer (D) (part(s))	Acid generator (B) (part(s))	Acid diffusion controller (part(s))	Additive (part(s))	Organic solvent (part(s))
Ex. 20	A14(100)	-	B(3)	E(0.05)	-	C2(150)
Ex. 21	A15(100)	-	B(3)	E(0.05)	-	C2(150)
Ex. 22	A16(100)	-	B(3)	E(0.05)	-	C2(150)
Ex. 23	A17(100)	-	B(3)	E(0.05)	-	C2(150)
Ex. 24	A18(100)	-	B(3)	E(0.05)	-	C2(150)
Ex. 25	A19(100)	-	B(3)	E(0.05)	-	C2(150)
Ex. 26	A20(100)	-	B(3)	E(0.05)	-	C2(150)
Ex. 27	A21(100)	-	B(3)	-	-	C2(100)
Ex. 28	A21(90)	-	B(3)	-	F(10)	C2(100)
Ex. 29	A21(80)	-	B(3)	-	F(20)	C2(100)
Ex. 30	A22(80)	-	B(3)	-	F(20)	C2(100)
Ex. 31	A23(80)	-	B(3)	-	F(20)	C2(100)
Ex. 32	A24(80)	-	B(3)	-	F(20)	C2(100)
Ex. 33	A25(80)	-	B(3)	-	F(20)	C2(100)

Table 2 (continued)

	Polymer (A) (part(s))	Polymer (D) (part(s))	Acid generator (B) (part(s))	Acid diffusion controller (part(s))	Additive (part(s))	Organic solvent (part(s))
Comp. Ex. 1	R1(100)	B1(20)	B(3)	-	-	C1(150)
Comp. Ex. 2	R1(100)	B1(30)	B(3)	-	-	C1(150)
Comp. Ex. 3	R1(100)	B2(20)	B(3)	-	-	C1(150)
Comp. Ex. 4	R2(100)	B1(20)	B(3)	-	-	C1(150)
Comp. Ex. 5	R3(100)	B1(20)	B(3)	-	-	C1(150)
Comp. Ex. 6	R1(100)	-	B(3)	-	-	C1(150)

Polymer (D) D3: polyvinyl methyl ether

Acid generator B: 4,7-di-n-butoxynaphthyltetrahydrothiophenium trifluoromethanesulfonate

Acid diffusion controller E: 2,4,6-tri(2-pyridyl)-s-triazine

5 Additive F: 4,4'-[1-[4-[2-(4-hydroxyphenyl)-2-propyl]phenyl]ethylene]bisphenol

Organic solvent C1: ethyl lactate, C2: propylene glycol monomethyl ether acetate

Table 3

	Sensitivity (mJ/cm ²)	Resolution	Dimensional fidelity of pattern Wt/Wb (μm)	Crack resistance	Shape of plated portion	Dimensional fidelity of plated portion Wt/Wb (μm)
Ex. 1	400	AA	30.1 / 29.7	AA	AA	30.8 / 30.5
Ex. 2	400	AA	30.3 / 29.7	AA	AA	31.5 / 30.9
Ex. 3	500	AA	30.4 / 29.5	AA	AA	30.8 / 30.3
Ex. 4	600	AA	31.1 / 29.8	AA	AA	31.4 / 30.2
Ex. 5	400	AA	31.3 / 30.0	AA	AA	31.5 / 30.2
Ex. 6	400	AA	31.5 / 29.4	AA	AA	32.9 / 31.2
Ex. 7	400	AA	30.3 / 29.1	AA	AA	30.5 / 29.6
Ex. 8	300	AA	31.1 / 28.8	AA	BB	31.9 / 29.6
Ex. 9	300	AA	31.4 / 29.4	AA	BB	31.4 / 29.8
Ex. 10	400	AA	30.6 / 29.7	AA	AA	30.4 / 30.4
Ex. 11	400	AA	31.1 / 30.2	AA	AA	31.6 / 30.8
Ex. 12	1000	AA	31.5 / 30.4	AA	AA	31.4 / 31.0
Ex. 13	1500	AA	29.6 / 29.8	AA	AA	30.0 / 30.6
Ex. 14	2000	AA	30.0 / 29.5	AA	BB	31.0 / 30.6
Ex. 15	1000	BB	30.5 / 29.1	AA	AA	30.8 / 30.1
Ex. 16	250	AA	29.5 / 29.9	AA	AA	30.0 / 30.3
Ex. 17	300	AA	29.0 / 30.1	AA	AA	29.8 / 30.4

Table 3 (continued)

	Sensitivity (mJ/cm ²)	Resolution	Dimensional fidelity of pattern Wt/Wb (μm)	Crack resistance	Shape of plated portion	Dimensional fidelity of plated portion Wt/Wb (μm)
Ex. 18	300	AA	30.2 / 30.1	AA	AA	30.4 / 30.4
Ex. 19	350	AA	30.6 / 29.8	AA	AA	30.2 / 30.0
Ex. 20	450	AA	31.3 / 29.7	AA	AA	30.8 / 30.0
Ex. 21	450	AA	30.3 / 29.7	AA	AA	30.3 / 29.7
Ex. 22	500	AA	31.0 / 30.5	AA	AA	30.1 / 30.7
Ex. 23	450	AA	29.7 / 29.1	AA	AA	29.1 / 29.8
Ex. 24	500	AA	28.0 / 30.1	AA	AA	28.1 / 30.1
Ex. 25	600	AA	29.1 / 31.1	AA	AA	30.1 / 31.6
Ex. 25	600	AA	30.4 / 31.0	AA	AA	30.4 / 31.0
Comp. Ex. 1	300	AA	30.6 / 29.4	AA	BB	31.8 / 31.1
Comp. Ex. 2	300	BB	30.6 / 29.2	AA	BB	31.2 / 30.8
Comp. Ex. 3	300	AA	31.1 / 30.2	AA	BB	31.2 / 31.8
Comp. Ex. 4	400	AA	31.2 / 30.6	BB	BB	32.0 / 31.8
Comp. Ex. 5	500	AA	31.4 / 30.6	BB	BB	32.0 / 31.8

Table 4

	Sensitivity (mJ/cm ²)	Resolution	Abnormality of pattern shape	Wettability by plating solution	Plating solution resistance
Ex. 27	2,000	AA	AA	BB	AA
Ex. 28	1,800	AA	AA	BB	AA
Ex. 29	1,500	AA	AA	BB	AA
Ex. 30	1,300	AA	AA	AA	AA
Ex. 31	1,000	AA	AA	AA	AA
Ex. 32	800	AA	AA	AA	AA
Ex. 33	1,500	AA	AA	AA	AA
Comp. Ex. 6	BB	-	-	-	-